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Transport properties of substitutionally disordered alloys

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A unified theoretical treatment of single-particle, e.g., density of states, and two-particle, e.g., transport properties of substitutionally disordered alloys, is presented using the embedded-cluster method (ECM) within the coherent-potential approximation. Comparison with results of exact numerical simulations of the ac conductivity shows that the ECM allows for the proper inclusion of vertex corrections and provides a reliable and accurate technique for determining the transport properties of alloys.

Recent theoretical studies of disordered materials have concentrated mostly on the calculation of the single-particle properties, e.g., the density of states (DOS), of substitutionally disordered alloys. Comparatively less attention has been given to the two-particle-related properties, e.g., transport phenomena such as electric conductivity, thermopower, etc., due to the greater difficulty in calculating two-particle Green's functions and the associated vertex corrections. Vertex corrections arise from the simultaneous interaction of two particles with the same configuration of the system. It is the purpose of this paper to demonstrate that transport properties, in particular the ac conductivity of concentrated, substitutionally disordered alloys, including vertex corrections, can be calculated as efficiently and accurately as single-particle properties within a well understood and established analytic cluster method. This approach has a number of virtues including becoming exact in the large-cluster-size limit, allowing the investigation of the effects of short-range order, and being applicable to tight-binding and muffin-tin Hamiltonians.

Of all proposed single-site theories, the coherent-potential approximation[1-4] (CPA) provides unquestionably the best method for the calculation of one-particle Green's functions and related quantities in substitutionally disordered alloys. In addition, the CPA provides[5-8] a first approximation to the calculation of two-particle Green's functions in these systems. However, in spite of its many desirable properties, the CPA, as a single-site theory, cannot account for the effects of statistical fluctuations in the environment of a site. Consequently, its accuracy decreases[9] with increasing disorder, scattering strength, or increasing short-range order (SRO), i.e., nonrandomness in a material.

In order to account for the effects of local statistical fluctuations it is necessary to extend the CPA to a multisite or cluster theory. Several such theories have been proposed which include both self-consistent[10,11] and non-self-consistent[12,13] approaches. The molecular CPA (Ref. 10) (MCPA) forms the natural cluster generalization of the single-site CPA, possesses many desirable properties, such as complete self-consistency and analyticity, and has been generalized[14] to the calculation of transport properties. As is well known, however, the MCPA suffers from two major drawbacks. First, with increasing cluster size the method becomes computationally extremely difficult. Second, it requires the introduction of a superlattice which violates the translational invariance of the underlying lattice and may lead to spurious gaps in the spectral functions near the edges of the associated Brillouin zone.

The second self-consistent cluster theory[11] referred to here, the traveling cluster approximation (TCA), preserves the translational symmetry of the underlying lattice and yields analytic results for the alloy self-energy and Green's function. It has also been shown[11] to yield accurate DOS's for some alloys. However, the numerical implementation of the TCA becomes prohibitively difficult even for moderate size clusters in simple, one-band disordered systems. In addition, the TCA is apparently inapplicable to nonrandom alloys. Finally, an application of the TCA to the calculation of transport phenomena has not been reported. Although the TCA remains a promising theory, a great deal more work is required to establish its validity and the limits of its reliability.

Since self-consistent cluster theories have not yet been very successful in the calculation of one-particle Green's functions or of transport properties, the search has been directed toward the construction of non-self-consistent methods. Of these, the embedded-cluster method[12,13] (ECM) has proved the most successful in calculating one-particle properties of substitutionally disordered alloys. The ECM addresses and solves exactly the problem of treating a compact cluster of atoms embedded in a given medium. The ECM is characterized by several desirable properties: First, for a given analytic medium the ECM yields analytic results, i.e., preserves the Herglotz property of the medium Green's function. Second, it is applicable[9] to nonrandom alloys and can also be applied to alloy surfaces[15] as well as to three-dimensional ordered or disordered systems. Finally, the method is computationally practicable, allowing calculations in either model tight-binding (TB), single-band systems, or in realistic materials describable by muffin-tin (MT) potentials.[16] As we show in this paper, the ECM can also be used to calculate accurate ac conductivity spectra by treating exactly compact clusters of atoms in a disordered alloy. Thus the ECM provides a unified technique for calculating both one- and two-particle properties of substitutionally disordered systems.

Traditionally, it has been the comparison of analytically obtained DOS's of one-dimensional disordered chains with their exact numerically simulated counterparts which has pointed out the advantages as well as inadequacies of various approximations and sorted out their validity and reliability. Thus far no corresponding comprehensive comparisons have been reported for transport quantities.

Although the method to be presented is more generally applicable, we confine our discussion to a material describable by a single-band TB Hamiltonian of the well-known form,

$$H=\sum_i \epsilon_i c_i^\dagger c_i+\sum_{i\neq j} W_{ij} c_i^\dagger c_j \ . \tag{1}$$

Here, i refers to a site in the lattice, ϵ_i is a site energy, and W_{ij} is an intersite overlap (hopping) integral. In a binary alloy, $A_C B_{1-C}$, with diagonal disorder, ϵ_i can assume the "values" ϵ_A or ϵ_B with corresponding probability C or $1-C$. For simplicity we assume that W_{ij} is independent of the chemical occupation of sites i and j. Because numerical results are easiest to obtain in the case of one-dimensional systems we confine our discussion to binary, disordered linear chains. The generalization to higher-dimensional systems is straightforward. Within the framework of linear response theory, the real part of the ac conductivity of a one-dimensional system of length L can be expressed[17] in the forms,

$$\sigma(\omega)=\frac{2\pi e^2}{L}\omega\sum_{\gamma,\beta}(f_\gamma-f_\beta)|\langle\gamma|x|\beta\rangle|^2\delta(\hbar\omega+E_\gamma-E_\beta) \ , \tag{2a}$$

or

$$\sigma(\omega)=\frac{2\pi e^2}{\omega L}\sum_{\alpha,\beta}(f_\alpha-f_\beta)|\langle\alpha|v|\beta\rangle|^2\delta(\hbar\omega+E_\alpha-E_\beta) \ . \tag{2b}$$

Here $|\alpha\rangle$ and E_α are the eigenvectors of H and the corresponding eigenvalues, f_α is a Fermi function for a particular choice of the chemical potential, x is the position operator, and $v=\dot{x}$ is the velocity operator.

Equations (2a) and (2b) are very convenient for the performance of exact numerical simulations. Following the method of Alberts and Gubernatis,[18] we computed the eigenvalues and eigenvectors of finite segments of disordered chains with fixed boundary conditions and averaged the resulting conductivity spectra. Each linear segment consisted of 500 sites and for random diagonally disordered alloys stable average spectra were obtained with 20 segments.

The analytic calculation of the ac conductivity requires the evaluation of averages of two-particle quantities of the form $\langle GJGJ\rangle$. Here G is the single-particle Green's function which depends on the configuration of the alloy, J is the current operator, and the symbol $\langle\cdots\rangle$ denotes an average over all configurations. The current operator, J can also be configuration dependent, e.g., for MT systems,[19] but is independent of configuration in the simple TB model considered here.

The standard approximation in the calculation of two Green's-function averages is to replace averages of products by products of averages and attempt an independent calculation of the vertex corrections, $\langle GJGJ\rangle-\langle G\rangle J\langle G\rangle J$. In the CPA or the MCPA, the averages, $\langle G\rangle$, are in turn to be replaced by the corresponding effective-medium Green's functions. It can easily be shown[5] that the vertex corrections vanish within the CPA for the case of single-band TB materials. For multiband alloys, the current operator contains site-diagonal elements and a contribution to vertex corrections can be obtained[19,20] within the CPA. Vertex corrections can also be calculated[14] within a cluster theory such as the MCPA. However, the resulting conductivity spectra do not nearly display the rich structure observed in their exact computer-simulated counterparts for one-dimensional systems. Thus, we are led to consider methods which avoid the approximate replacement of $\langle GJGJ\rangle$ by $\langle G\rangle J\langle G\rangle J$, and instead calculate averages of products directly.

This program can be accomplished to any desired level of approximation within the framework of the ECM. The essence of the method is to calculate exactly the average $\langle G^C J G^C J\rangle_C$, where G^C is the Green's function associated with a cluster of atoms embedded in a CPA medium, and $\langle\cdots\rangle_C$ denotes an average over all cluster configurations. Here, the cluster Green's function is given by the expression,

$$G^C=(z-H_C-\Delta_C)^{-1} \ , \tag{3}$$

where H_C is the intracluster Hamiltonian for a particular configuration, and Δ_C denotes the (configuration-independent) interaction of the cluster with the surrounding medium. In terms of these cluster Green's functions the real part of the ac conductivity can be written in the form (with $2e^2=1$),

$$\begin{aligned}\sigma(\omega)&=\frac{1}{\pi^2\omega}\int_{\mu-\omega}^{\mu}dE\,\langle[\mathrm{Im}G^C(E)J\,\mathrm{Im}G^C(E+\hbar\omega)J]_{00}\rangle_C\\&=\frac{1}{\pi^2\omega}\int_{\mu-\omega}^{\mu}dE\left\langle\sum_{i,j,k\in C}\mathrm{Im}G^C_{0i}(E)J_{ij}\,\mathrm{Im}G^C_{jk}(E+\hbar\omega)J_{k0}\right\rangle_C \ .\end{aligned} \tag{4}$$

The indices i,j,k in this equation are confined to the cluster C and 0 denotes the center of the cluster.

The following figures depict the results of numerical calculations. In Fig. 1 we compare exact DOS's (histogram) for a one-dimensional substitutionally disordered alloy, with DOS's obtained in the CPA (dotted curve) and in a seven-

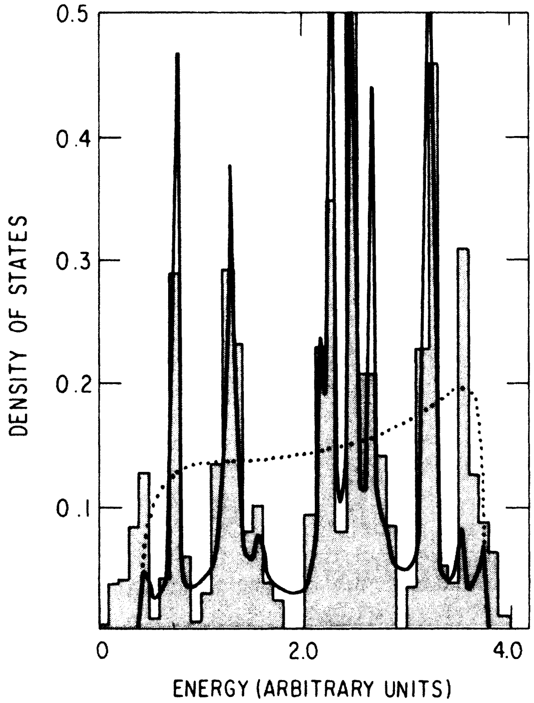

FIG. 1. Exact numerically simulated densities of states (shaded histogram) for a one-dimensional binary alloy with only diagonal disorder compared with the DOS's obtained in the CPA (dotted curve) and in a seven-site application of the ECM (solid curve). The spectra are symmetric about $E=0.0$.

site cluster application of the ECM (solid curve). It is seen that the ECM yields quite accurate DOS's away from the band edges even for moderate size clusters. The rather poor performance of the ECM near the edges of the band is due to the choice of a single-site CPA medium which, as is clearly seen in Fig. 1, yields a band narrower than the exact one. Much more accurate DOS's are obtained,[9] even in the case of alloys exhibiting SRO, if the medium is constructed to contain self-consistently local environment fluctuations in the vicinity of a site. The effect on the conductivity of more proper choices of an embedding medium will be examined critically in a forthcoming publication.[8]

Figure 2 depicts the exact ac conductivity spectrum (histogram) for the alloy of Fig. 1 with the chemical potential chosen in the middle of the band $\mu = 0.5$ ($E = 0.0$), and the corresponding results obtained in the CPA (dotted curve) as well as in the ECM (solid curve). Not unexpectedly the CPA yields a smooth conductivity curve in sharp contrast to the highly structured exact spectrum. On the other hand, the results obtained in a seven-site ECM calculation on the basis of Eq. (4) contain a great deal of structure which resolves practically all peaks in the exact curve. Somewhat surprisingly, a seven-site ECM calculation of the conductivity appears to yield comparatively more accurate results than it does for the DOS. In particular, there appears to exist no deleterious effects due to the poor performance of the ECM near the edges of the band. This result, however, is not hard to understand. The ac conductivity involves the convolution of two DOS curves and consequently contains less structure than either of them. On the other hand, a seven-site ECM calculation retains the dominant peaks in the DOS, i.e., those which can be expected to survive the convolution process.

It is to be noted that a calculation based on relatively small clusters yields accurate results for quantities which, in principle, can be expected to be influenced by distant fluctuations. This is due to the fact that increasing disorder localizes the wave functions in the material and diminishes the importance of fluctuations beyond a moderate distance. By contrast, no finite cluster calculation can be expected to yield accurate results for the DOS or the transport quantities of ordered materials. Furthermore, in alloys exhibiting strong SRO effects a much more judicious choice of an embedding medium may be necessary,[8,9] coupled with possibly larger cluster sizes, before accurate results can be obtained.

The method presented here has several desirable features. First, it allows the incorporation from the start of local fluctuations into the conductivity formula and avoids the calculation of vertex corrections at a later stage. Second, it becomes exact in the limit of large cluster sizes (and appropriately chosen embedding media). Third, it allows the investigation of the effects of short-range order (nonrandomness) since, as was the case with DOS calculations, it enables one to indentify peaks in the conductivity spectra with specific local atomic configurations.[8] Fourth, the method is computationally simple and can be applied to disordered materials in any dimension and to alloys describable by TB as well as MT Hamiltonians. In fact, since realistic systems can, in general, be expected to possess less structured spectra than those of model 1D alloys, the ECM can be used to advantage in such systems with rather small clusters, such as tetrahedra in an fcc lattice. Larger clusters may, however, be necessary in order to account for SRO effects in real materials. Finally, this approach brings the calculation of transport properties of disordered materials on a par with those of the DOS within the same, unified formalism.

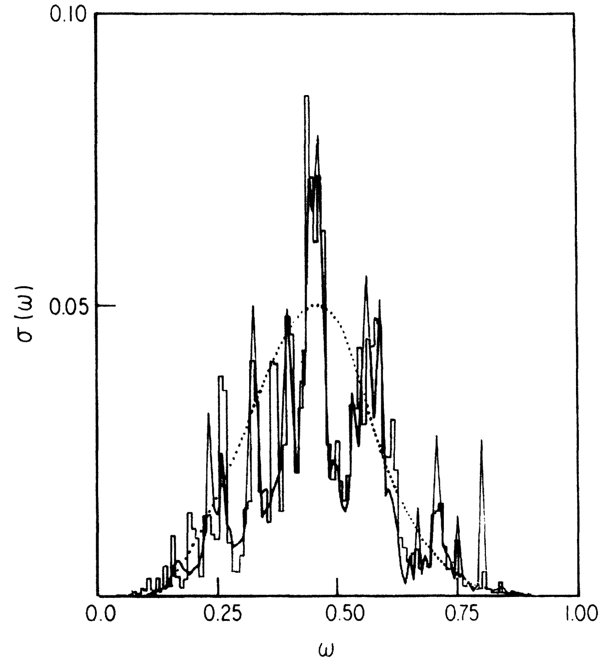

FIG. 2. Exact numerically simulated ac conductivity (shaded histogram) for a one-dimensional binary alloy compared with the conductivity obtained in the CPA (dotted curve) and in a seven-site application of the ECM (solid curve). Frequency in units of the bandwith.

Having exhibited the desirable properties of the ECM in connection with the calculation of conductivity spectra, we must caution that the method should not be construed as the final word on the subject. As already mentioned, any ECM calculation with moderate size clusters is strongly dependent on the choice of the embedding medium. For random alloys, the CPA has been shown to provide an acceptable medium for embedding the cluster, but more sophisticated choices may be necessary in order to account for strong SRO effects. Thus, the need still exists for a fully self-consistent cluster theory, such as perhaps the TCA,[21] which would prescribe the choice of the medium and allow the treatment of SRO within the same formalism. The ECM, on the other hand, although not cluster self-consistent, provides a straightforward, conceptually clear, and computationally efficient method for the calculation of densities of states as well as transport quantities in substitutionally disordered alloys and may form the starting point in the construction of a fully satisfactory alloy theory.

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[1] P. Soven, Phys. Rev. **156**, 809 (1967).

[2] P. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. **46**, 465 (1974), and references therein.

[3] B. L. Gyorffy and G. M. Stocks, in *Electrons in Disordered Metals and Metallic Surfaces,* edited by P. Phariseau, B. L. Gyorffy, and L. Scheire (Plenum, New York, 1978), p. 89, and references therein.

[4] J. S. Faulkner, in *Progress in Material Science,* edited by J. W. Christian, P. Hassen, and T. B. Massalski (Pergamon, New York, 1982), Vols. 1 and 2, and references therein.

[5] B. Velicky, Phys. Rev. **185**, 614 (1969).

[6] J. A. Blackman, Phys. Rev. B **12**, 3482 (1975).

[7] G. M. Stocks and W. H. Butler, Phys. Rev. Lett. **48**, 55 (1982).

[8] M. Hwang, A. Gonis, and A. J. Freeman (unpublished).

[9] A. Gonis and A. J. Freeman, Phys. Rev. **29**, 4277 (1984).

[10] M. Tsukada, J. Phys. Soc. Jpn. **32**, 1475 (1972).

[11] R. Mills and P. Ratanavararaksa, Phys. Rev. B **18**, 5291 (1978).

[12] A. Gonis and J. W. Garland, Phys. Rev. B **16**, 2474 (1977).

[13] Charles W. Myles, and John D. Dow, Phys. Rev. Lett. **42**, 254 (1979).

[14] G. Czycholl and J. Zittartz, Z. Phys. B **30**, 375 (1978).

[15] M. Hwang, R. Podloucky, A. Gonis, and A. J. Freeman (unpublished).

[16] A. Gonis, W. H. Butler, and G. M. Stocks, Phys. Rev. Lett. **50**, 1482 (1983).

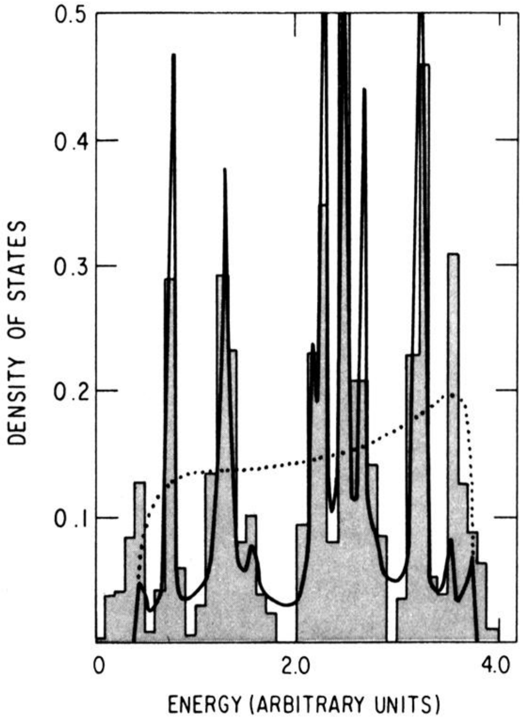
[17] D. J. Thouless, Phys. Rep. **13**, 93 (1974).

[18] R. C. Alberts and J. E. Gubernatis, Phys. Rev. B **17**, 4487 (1978).

[19] L. Schwartz, Phys. Rev. B **24**, 1091 (1981).

[20] W. H. Butler, Phys. Rev. B **31**, 3260 (1985).

[21] L. J. Gray and T. Kaplan, Phys. Rev. B **24**, 1872 (1981).



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